



PATENT COOPERATION TREATY
PCT
INTERNATIONAL PRELIMINARY EXAMINATION REPORT
(PCT Article 36 and Rule 70)

Applicant's or agent's file reference P200025	FOR FURTHER ACTION See Notification of Transmittal of International Preliminary Examination Report (Form PCT/PEA/416)	
International application No. PCT/EP 02/1258	International filing date (day/month/year) 08.10.2002	Priority date (day/month/year) 08.10.2002
International Patent Classification (IPC) or both national classification and IPC C08K5/00		
Applicant BOREALIS TECHNOLOGY OY et al		

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.
2. This REPORT consists of a total of 4 sheets, including this cover sheet.
- ☒ This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).
- These annexes consist of a total of 8 sheets.

3. This report contains indications relating to the following items:
- I ☒ Basis of the opinion
 - II ☐ Priority
 - III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
 - IV ☐ Lack of unity of invention
 - V ☒ Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
 - VI ☐ Certain documents cited
 - VII ☐ Certain defects in the international application
 - VIII ☐ Certain observations on the international application

Date of submission of the demand 25.03.2004	Date of completion of this report 17.01.2005
Name and mailing address of the international preliminary examining authority:  European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465	Authorized Officer Sperry, P Telephone No. +49 89 2399-8298 

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT**

International application No. PCT/EP 02/11258

I. Basis of the report

1. With regard to the **elements** of the international application (*Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17)*):

Description, Pages

1-22 as originally filed

Claims, Numbers

1-20 filed with telefax on 20.12.2004

Drawings, Sheets

1/1 as originally filed

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

These elements were available or furnished to this Authority in the following language: , which is:

- ☐ the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).
☐ the language of publication of the international application (under Rule 48.3(b)).
☐ the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

- ☐ contained in the international application in written form.
☐ filed together with the international application in computer readable form.
☐ furnished subsequently to this Authority in written form.
☐ furnished subsequently to this Authority in computer readable form.
☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. The amendments have resulted in the cancellation of:

- ☐ the description, pages:
☐ the claims, Nos.:
☐ the drawings, sheets:

**INTERNATIONAL PRELIMINARY
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5. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)).

(Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)

6. Additional observations, if necessary:

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes: Claims	1-20
	No: Claims	
Inventive step (IS)	Yes: Claims	1-20
	No: Claims	
Industrial applicability (IA)	Yes: Claims	1-20
	No: Claims	

2. Citations and explanations

see separate sheet

Re Item V

**Reasoned statement with regard to novelty, inventive step or industrial applicability;
citations and explanations supporting such statement**

Reference is made to the following documents:

- D1: DATABASE WPI Section Ch, Week 200138 Derwent Publications Ltd., London, GB; Class A17, AN 2001-365817 XP002243985 & RU 2 166 217 C (REAL SERVICE CABLE CORP) 27 April 2001 (2001-04-27)
D2: EP-A-0 827 979 (IDEMITSU KOSAN CO) 11 March 1998 (1998-03-11)

1. Document D1 relates to an electric insulation compound containing 0.13-0.53 mass.% Irganox 1010TM (pentaerythritol-tetra[3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionate]; 0.06-0.27 mass.% Irgafos 168TM (tris(2,4-di-t-butylphenyl) phosphite) 0.10-0.40 Irganox PS 802 (distearyl thiodipropionate), in a propylene block copolymer with ethylene. A phosphorous compound as claimed in claim 1 of the present application is not disclosed in D1.
2. Document D2 relates to a stabilized polystyrene composition having improved resistance to heat aging. The composition comprises 100 parts by weight of the resin of a polystyrenic resin 1, 0.005 to 5.0 parts by weight of a phenolic antioxidant, 0.005 to 5.0 parts by weight of an antioxidant containing phosphorus, and 0.005 to 5.0 parts by weight of an antioxidant containing sulfur. in tables 5A, 6A, 7A and 8A numerous examples are described in which the antioxidants of the application present are described. Further antioxidants such as distearyl pentaerythritol diphosphite are mentioned in the description (p. 7, l. 26-27). However polystyrene does not belong to the class of polyolefin despite the fact that both contains carbon-to-carbon double bonds.
3. The claimed composition is characterized in that specific phosphorous compounds are used. At least for one of these four phosphorous compounds an unexpected effect has been shown by the applicant. Apparently bis(2,4-dicumylphenyl)pentaerythritol diphosphite improves the long term heat stability (LTHS) properties of the polymer with respect to tris(2,4-di-t-butylphenyl) phosphite (see Figure 1 and 2) which has been used in D1.

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International Patent Application PCT/EP02/11258

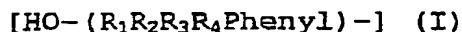
Borealis Technology Oy et al.

New claims:

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1. A stabilized polymer composition comprising a polyolefin and an antioxidant composition for improving the long term heat stability of polyolefins, said antioxidant composition comprising:

- 10 (a) 0,01% - 0,5% by weight of at least one sterically hindered phenolic compound, wherein said phenolic compound contains at least one phenolic moiety of general formula (I):



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wherein R_1 , R_2 , R_3 or R_4 may be the same or different and at least one of R_1 , R_2 , R_3 or R_4 is selected from the group consisting of branched alkyl having 1 to 12 carbon atoms, preferably tert.-butyl, iso-propyl, cyclohexyl, cyclopentyl and adamantyl, the others of R_1 , R_2 , R_3 or R_4 being H or lower alkyl having 1 to 6 carbon atoms;

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(b) 0,01% - 0,5% by weight of at least one phosphorous compound, wherein said phosphorous compound is selected from the group consisting of:

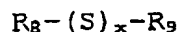
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- Tetrakis-(2,4-di-t-butylphenyl)-4,4'-biphenylen-di-phosphonite;
- Bis(2,6-di-t-butyl-4-methylphenyl)pentaerythrityl-di-phosphite;
- 30 - Di-stearyl-pentaerythrityl-di-phosphite; and
- Bis(2,4-dicumylphenyl)pentaerythritol diphosphite;

(c) 0,01% - 1% by weight of at least one sulphur-containing compound of general formula (III):

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(III)

wherein $x = 1$ or 2 , and wherein R_8 and R_9 may be the same or different and are selected from the group consisting of C_{10} -

5 C_{25} alkyl groups optionally being substituted with C_1 - C_{12} alkyl ester carboxylates, wherein said % by weight values are referred to the polymer composition.

10 2. A stabilized polymer composition according to claim 1, comprising a polyolefin and an antioxidant composition, wherein said antioxidant composition comprises:

(a) 0,02% - 0,2% by weight of said at least one sterically hindered phenolic compound,

15 (b) 0,03% - 0,2% by weight of said at least one phosphorous compound, and

(c) 0,05% - 0,6% by weight of said at least one sulphur-containing compound of general formula (III), wherein said % by weight values are referred to the polymer
20 composition.

3. A stabilized polymer composition according to claim 1, comprising a polyolefin and an antioxidant composition, wherein said antioxidant composition comprises:

25 (a) 0,03% - 0,15% by weight of said at least one sterically hindered phenolic compound,

(b) 0,05% - 0,15% by weight of said at least one phosphorous compound, and

(c) 0,1% - 0,5% by weight of said at least one sulphur-containing compound of general formula (III), wherein said % by weight values are referred to the polymer
30 composition.

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4. The stabilized polymer composition of any of claims 1 to 3, wherein the phenolic compound contains at least one phenolic moiety of general formula (Ia):

5 HO-(R₁R₂R₃R₄Phenyl)-W (Ia)

wherein R₁ and R₄ being in the 2- and 6-position of the phenol residue may be the same or different and are selected from the group consisting of preferably branched C₁ to C₁₂ alkyl, particularly tert.-butyl, iso-propyl, cyclohexyl, cyclopentyl and adamantyl residues, R₂ and R₃ having the meaning as given before, and W is selected from C₁ to C₁₂ alkyl, C₁ to C₁₂ alkoxy, C₁ to C₁₂ alkyl carboxylate or C₁ to C₁₂ alkyl substituted by another group of the formula HO-(R₁R₂R₃R₄Phenyl)-, wherein R₁ to R₄ have the meaning as indicated before.

5. The stabilized polymer composition of any of claims 1 to 4, wherein the sulphur-containing compound of general formula (III):



is selected from Di(C₁-C₂₀)alkyl-(S)_x-di-carboxylate wherein the carboxylic acid is selected from C₁ to C₁₂ alkyl carboxylic acids.

6. The stabilized polymer composition of any of the preceding claims, wherein the sterically hindered phenolic compound is selected from the group consisting of:

- 2,6-Di-tert.-butyl-4-methyl phenol;
- Pentaerythrityl-tetrakis(3-(3',5'-di-tert.-butyl-4-hydroxyphenyl)-propionate;
- Octadecyl 3-(3',5'-di-tert.-butyl-4-hydroxyphenyl)propionate;

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- 1,3,5-Trimethyl-2,4,6-tris-(3,5-di-tert.-butyl-4-hydroxyphenyl) benzene;

- 2,2'-Thiodiethylene-bis-(3,5-di-tert.-butyl-4-hydroxyphenyl)-propionate;

5 - Calcium-(3,5-di-tert.-butyl-4-hydroxy benzyl monoethyl-phosphonate);

- 1,3,5-Tris(3',5'-di-tert.-butyl-4'-hydroxybenzyl)-isocyanurate;

- Bis-(3,3-bis-(4'-hydroxy-3'-tert.-butylphenyl) butanoic acid)-glycolester;

- 4,4'-Thiobis (2-tert.-butyl-5-methylphenol);

- 2,2'-Methylene-bis(6-(1-methyl-cyclohexyl)para-cresol);

- N,N'-hexamethylene bis(3,5-di-tert. Butyl-4-hydroxy-hydrocinnamamide;

15 - 2,5,7,8-Tetramethyl-2(4',8',12'-trimethyltridecyl)chroman-6-ol;

- 2,2'-Ethylidenebis(4,6-di-tert.-butylphenol);

- 1,1,3-Tris(2-methyl-4-hydroxy-5-tert.-butylphenyl)butane;

20 - 1,3,5-Tris(4-tert.-butyl-3-hydroxy-2,6-dimethylbenzyl)-1,3,5-triazine-2,4,6-(1H,3H,5H)-trione;

- 3,9-Bis(1,1-dimethyl-2-(beta-(3-tert.-butyl-4-hydroxy-5-methylphenyl)propionyloxy)ethyl)-2,4,8,10-tetraoxaspiro(5,5)undecane;

25 - 1,6-Hexanediyl-bis(3,5-bis(1,1-dimethylethyl)-4-hydroxybenzene-propanoate);

- 2,6-Di-tert.-butyl-4-nonylphenol;

- 3,5-Di-tert.-butyl-4-hydroxyhydrocinnamic acid triester with 1,3,5-tris (2-hydroxyethyl)-s-triazine-2,4,6(1H,3H,5H)-trione;

30 - 4,4'-Butylidenebis(6-tert. Butyl-3-methylphenol);

- 2,2'-Methylene bis (4-methyl-6-tert.-butylphenol);

- 2,2-Bis(4-(2-(3,5-di-t-butyl-4-hydroxyhydrocinnamoyloxy))ethoxyphenyl))propane;

- 5 -

- Triethyleneglycol-bis-(3-tert.-butyl-4-hydroxy-5-methylphenyl) propionate;
- Benzenepropanoic acid, 3,5-bis(1,1-dimethylethyl)-4-

hydroxy-, C₁₃-C₁₅-branched and linear alkyl esters;

- 5 - 6,6'-Di-tert.-butyl-2,2'-thiodi-p-cresol;
- Diethyl((3,5-bis(1,1-dimethylethyl)-4-hydroxyphenyl)methyl) phosphonate;
- 4,6-Bis(octylthiomethyl)o-cresol;
- Benzenepropanoic acid, 3,5-bis(1,1-dimethylethyl)4-
- 10 hydroxy-, C₇-C₉-branched and linear alkyl esters;
- 1,1,3-Tris[2-methyl-4-[3-(3,5-di-t-butyl-4-hydroxyphenyl)propionyloxy]-5-t-butylphenyl] butane; and
- Butylated reaction product of p-cresol and dicyclopentadiene.

15

7. The stabilized polymer composition of any of the preceding claims, wherein the sulphur-containing compound is selected from the group consisting of:

- Di-stearyl-thio-di-propionate;
- 20 - Di-palmityl/stearyl-thio-di-propionate;
- Di-lauryl-thio-di-propionate;
- Di-tridecyl-thio-di-propionate;
- Di-myristyl-thio-di-propionate;
- Pentaerythritol octyl thiodipropionate;
- 25 - Lauryl-stearyl-thio-di-propionate;
- Di-octadecyl-disulphide;
- Di-tert-dodecyl-disulphide and
- Pentaerythritol-tetrakis-(3-laurylthiopropionate)

30

8. The stabilized polymer composition of any of the preceding claims, wherein the sterically hindered phenolic compound is selected from the group consisting of:

- Pentaerythrityl-tetrakis(3-(3',5'-di-tert.-butyl-4-hydroxyphenyl)-propionate;

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- Octadecyl 3-(3',5'-di-tert.-butyl-4-hydroxyphenyl)propionate;
- 1,3,5-Trimethyl-2,4,6-tris-(3,5-di-tert.-butyl-4-hydroxyphenyl) benzene;
- 5 - 1,3,5-Tris(3',5'-di-tert.-butyl-4'-hydroxybenzyl)-isocyanurate;
- Bis-(3,3-bis-(4'-hydroxy-3'-tert.-butylphenyl)butanoic acid)-glycolester; and
- 10 - 3,9-Bis(1,1-dimethyl-2-(beta-(3-tert.-butyl-4-hydroxy-5-methylphenyl)propionyloxy)ethyl)-2,4,8,10-tetraoxaspiro(5,5)undecane.

9. The stabilized polymer composition of any of the preceding claims, wherein the sulphur-containing compound is
15 Di-stearyl-thio-di-propionate or Di-tert-dodecyl-disulphide.

10. The stabilized polymer composition of any of any of the preceding claims, wherein

(a) the sterically hindered phenolic compound is 1,3,5-
20 Tris(4-tert.-butyl-3-hydroxy-2,6-dimethylbenzyl)-1,3,5-triazine-2,4,6-(1H,3H,5H)-trione or pentaerythrityl-tetrakis(3-(3',5'-di-tert.-butyl-4-hydroxyphenyl)-propionate;

(b) the phosphite compound is bis(2,4-dicumylphenyl) pentaerythritol diphosphite; and

25 (c) the sulphur-containing compound is Di-stearyl-thio-di-propionate.

11. The stabilized polymer composition of any of claims 1-10, wherein said composition further comprises metal
30 deactivators and/or UV-stabilisers.

12. The stabilized polymer composition of claim 11, wherein said UV-stabilizers are sterically hindered amines.

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13. The stabilized polymer composition of any of the preceding claims, wherein said polyolefin is a homo- or co-polymer of polyethylene, polypropylene and polybutadiene.

5 14. Use of the antioxidant composition as defined in any of claims 1-11 for reducing degradation of a polyolefin material during processing and end use of said polyolefin material.

10 15. The use of claim 14 for increasing long term thermal stability of the polyolefin material.

15 16. Method for producing a polyolefin article having an improved long term thermal stability against ageing by radical degradation processes comprising the steps of:
 (a) providing an unstabilised base polyolefin material;
 (b) adding to said base polyolefin material the antioxidant composition as defined in any of the preceding claims;
20 (c) converting the composition obtained in step (b) in a melt-forming process; and
 (d) confectioning the polyolefin material obtained in step (c).

25 17. The method of claim 16 further comprising adding other stabilisers and/or modifiers before the converting step c).

30 18. The method of any of claims 16 or 17, wherein the converting step includes injection moulding, blow moulding, rotational moulding and extrusion.

35 19. The method of any of claims 16 to 18, wherein the confectioning step includes cutting, lamination and/or welding:

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20. Polyolefin article having an increased long term ageing stability obtained by the method of any of claims 20-

23.